

Effects of Added Anions on the Reaction of Nitrous Acid with Hydrogen Peroxide

Jong-Yoon Park*, Eun Jin Choi, and Joon Woo Park†

Department of Science Education and †Department of Chemistry, Ewha Womans University, Seoul 120-750

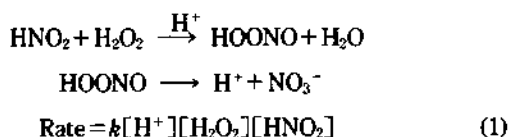
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The reactions of nitrous acid with hydrogen peroxide in acidic aqueous solution in the presence of several added anions have been studied at 0°C and pH 2-4 to investigate the nucleophilic catalysis of these anions. From the dependence of reaction rates on the anion concentrations, significant catalytic effects were found for Cl⁻, Br⁻, SCN⁻, in order of effect SCN⁻ ≈ Br⁻ > Cl⁻, while no observable effect was found for ClO₄⁻ and NO₃⁻. These results support O-nitrosation reaction is the rate-determining step and NOX formed in the presence of an anion (X⁻) also acts as a nitrosating agent and accelerates the overall reaction rate. The order of reactivity was found to be NOCl > NOBr > NO-SCN, which is consistent with the results of N-nitrosation and S-nitrosation reactions.

Introduction

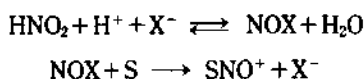
The reaction of nitrous acid with hydrogen peroxide in acidic aqueous solution has been widely studied because of its mechanistic interest¹⁻⁴ as well as its practical importance, e.g., enhancement of the absorption of nitrogen oxides in a wet scrubber for air pollution control⁵ and understanding the role of nitrous acid in cloud chemistry related with acid deposition phenomenon.^{6,7}

Early kinetic studies showed that this reaction is rapid and acid-catalysed, and that the reaction proceeds by nitrosation of peroxide oxygen to form peroxyxynitrous acid (HOONO) which rearranges to give a final product, nitric acid.¹⁻⁴



The suggested effective nitrosating reagents are nitrosium ion (NO⁺)^{2,3} or nitrous acidium ion (H₂NO₂⁺).^{1,4} Both of them are consistent with kinetic observations. However, they are kinetically indistinguishable and there has been no clear experimental evidence which differentiates between NO⁺ and H₂NO₂⁺ as the reactive species yet.⁸

Acidic solutions of nitrous acid also have been used for many other reactions involving N-, C-, O-, S-nitrosation.⁹ From the kinetic data, effective nitrosation species are suggested to be NO⁺, H₂NO₂⁺ or dinitrogen trioxide (N₂O₃) depending on the substrate and experimental conditions such as acidity and total nitrous acid concentration. In the presence of certain anions (X⁻), for example halides and SCN⁻, nitrosyl compounds (NOX) are formed and then act as nitrosating reagents, enhancing the reaction rate. This nucleophilic catalysis has been observed for the nitrosation of many substrates (S) in the acidic solutions of nitrous acid and it has been found that the catalytic effect depends on the reactivity of nitrosyl compound and its equilibrium concentration.⁹



$$\text{Rate} = k[\text{H}^+][\text{S}][\text{HNO}_2][\text{X}^-] \quad (2)$$

Nitrosation reaction of some substrates, for example hydrazoic acid (HN₃), hydrazine (NH₂NH₂), sulphamic acid (NH₂SO₃H), etc., is very rapid and the reaction rate is considered to reach at the encounter-controlled limit.^{10,11} These very reactive substances have been used as nitrous acid scavengers, both in laboratory experiments¹¹ and on the industrial scale.¹² Recently it has been pointed out that hydrogen peroxide is also suited for this purpose because its nitrosation rate is considered to be close to the encounter-controlled limit.⁸ If this reaction could be catalysed by adding proper anions, then H₂O₂ acts as a nitrous acid scavenger even better.

To investigate the nucleophilic catalysis in the reaction of nitrous acid with hydrogen peroxide in acidic aqueous solution, we have carried out a kinetic study of this reaction in the presence of added anions and the results are presented here.

Experimental

All materials were of reagent grade and were used without further purification. Glass-distilled deionized water was used for all of the experiments.

Kinetic measurements were carried out under pseudo-first-order conditions: H₂O₂ concentrations were in large excess of those of total nitrous acid ([N(III)] = [HNO₂] + [NO₂⁻]), with the initial ratio [H₂O₂]/[N(III)] being 20 or greater. The initial concentration of total nitrous acid was kept as low as possible ([N(III)]₀ ≤ 5 × 10⁻⁵ M) to avoid its self decomposition, 2HNO₂ → NO + NO₂ + H₂O.¹³ Each kinetic run was followed by monitoring the decrease of total nitrous acid concentration of the reaction mixture using aliquots taken at predetermined intervals. The aliquot was immediately mixed with a solution of sulfanilamide and N-(1-naphthyl)-ethylenediamine dihydrochloride to convert N(III) into azo dye.⁴ Then the absorbance of this solution was measured by Beckman DU-40 spectrophotometer at 537 nm. Five or six determinations of [N(III)] were made for each run.

The concentration of H₂O₂ in stock solution was determined by iodometry.¹⁴ pH was maintained constant using per-

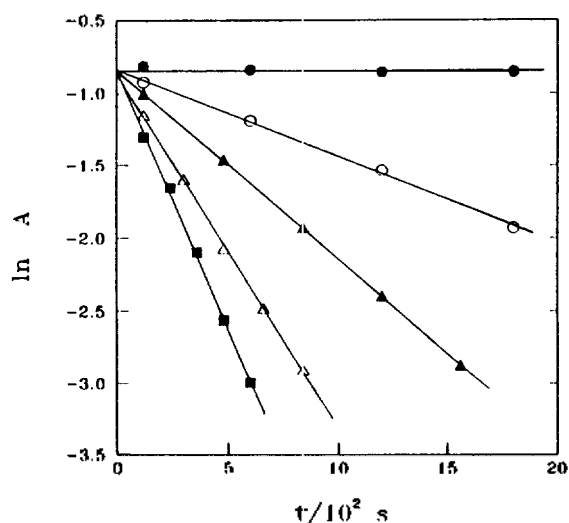


Figure 1. Typical pseudo-first-order plots of kinetic runs for the reaction of $\text{HNO}_2 + \text{H}_2\text{O}_2$ at pH 3.03 and 0°C . $[\text{N(III)}]_0 = 2.5 \times 10^{-5} \text{ M}$, $[\text{SCN}^-] = 0.1 \text{ M}$, $[\text{H}_2\text{O}_2]_0 = 0 \text{ M}$ (●); $0.5 \times 10^{-3} \text{ M}$ (○); $1 \times 10^{-3} \text{ M}$ (▲); $2 \times 10^{-3} \text{ M}$ (△); $3 \times 10^{-3} \text{ M}$ (■).

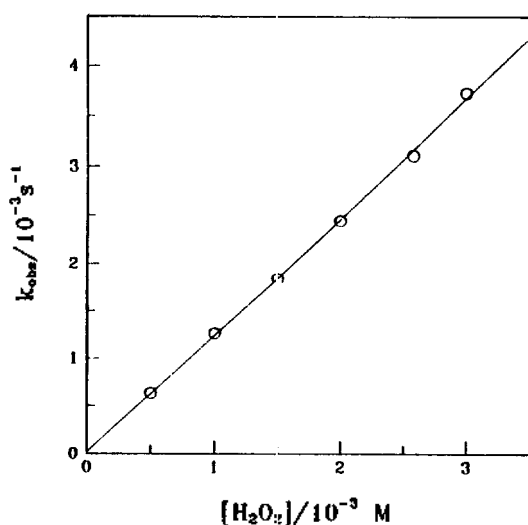


Figure 2. Dependence of k_{obs} on H_2O_2 concentrations for the reaction of $\text{HNO}_2 + \text{H}_2\text{O}_2$ in the presence of 0.10 M SCN^- at pH 3.03 and 0°C .

chloric acid or acetate buffer (for pH 3.87) and measured by a pH meter (Suntex Model-3000) equipped with a combination electrode (Ingold U402-S7). Ionic strength was adjusted to 0.5 M by adding NaClO_4 and reaction temperature was maintained at 0°C using an ice-water bath.

Results

All kinetic measurements showed a good first order dependence on the total nitrous acid concentration. Typical plots of \ln (Absorbance) versus time are shown in Figure 1. The pseudo-first-order rate constant, k_{obs} , was determined from the slope of the straight line fitted to the data points. Correlation coefficients of the linear regressions were usually higher than 0.995, and standard deviations of slopes were

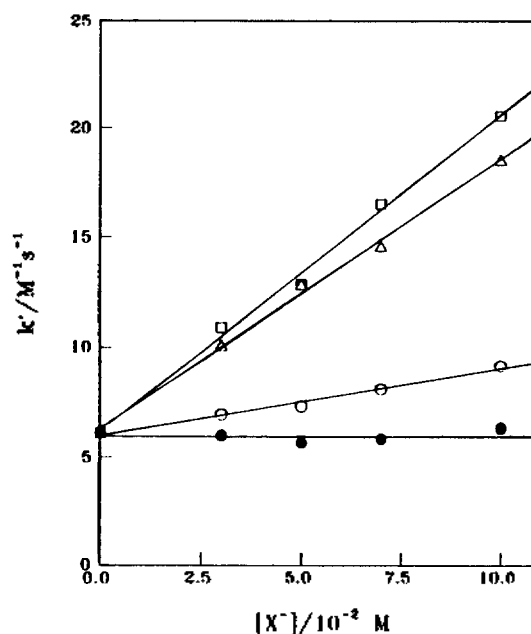


Figure 3. Plots of second-order rate constants vs. added anion concentrations for the reaction of $\text{HNO}_2 + \text{H}_2\text{O}_2$ at pH 2.08 and 0°C . $\text{X}^- = \text{NO}_3^-$ (●); Cl^- (○); Br^- (△); SCN^- (□).

Table 1. Second-Order Rate Constants Obtained for the Reaction of $\text{HNO}_2 + \text{H}_2\text{O}_2$ at pH 2.08 and 0°C . $[\text{H}_2\text{O}_2]_0 = 2.5 \times 10^{-4} \text{ M}$, $[\text{N(III)}]_0 = 1.25 \times 10^{-5} \text{ M}$

$[\text{X}^-]$	$k'/\text{M}^{-1}\text{s}^{-1}$			
	Cl^-	Br^-	SCN^-	NO_3^-
0.00	6.09	6.09	6.09	6.09
0.03	6.93	10.1	10.9	5.94
0.05	7.30	12.8	12.8	5.63
0.07	8.08	14.6	16.5	5.79
0.10	9.15	18.5	20.5	6.27
$k_o/\text{M}^{-1}\text{s}^{-1}$	5.99 ± 0.12	6.30 ± 0.26	6.18 ± 0.33	5.94 ± 0.11
$k_c/\text{M}^{-1}\text{s}^{-1}$	30.4 ± 2.0	122.5 ± 4.3	143.8 ± 5.5	

less than 3%. It was also found that the overall reaction rate is first order with respect to the concentration of hydrogen peroxide by observing the linear relationship in the plot of k_{obs} against $[\text{H}_2\text{O}_2]$ as shown in Figure 2. Thus the rate equation can be written as Eq. (3) and the second order rate constant k' can be calculated from $k_{\text{obs}}/[\text{H}_2\text{O}_2]$.

$$-d[\text{N(III)}]/dt = k_{\text{obs}} [\text{N(III)}] = k' [\text{H}_2\text{O}_2] [\text{N(III)}] \quad (3)$$

Second order rate constants obtained in this way are listed in the Tables 1-3 which show the dependence of k' on the concentrations of added anions for three different pHs. Each rate constant is the average of 2-4 measurements. A minor correction was made for the rate constant obtained at pH 3.87 since the acetate buffer used turned out to enhance the reaction rate. When the buffer concentration was doubled, the rate constant in the absence of added anion was increased by 16%. Thus all the rate constant obtained at pH 3.87 were corrected by subtracting this amount.

Table 2. Second-Order Rate Constants Obtained for the Reaction of $\text{HNO}_2 + \text{H}_2\text{O}_2$ at pH 3.03 and 0°C . $[\text{H}_2\text{O}_2]_0 = 1.0 \times 10^{-3} \text{ M}$, $[\text{N(II)}]_0 = 5.0 \times 10^{-5} \text{ M}$

[X ⁻]	$k'/\text{M}^{-1} \text{ s}^{-1}$		
	Cl ⁻	Br ⁻	SCN ⁻
0.00	0.354	0.354	0.354
0.10	0.644	1.33	1.31
0.20	0.945	2.09	2.16
0.30	1.10	2.98	3.23
0.40	1.46	3.98	3.98
0.50	1.70	4.86	5.13
$k_0/\text{M}^{-1} \text{ s}^{-1}$	0.367 ± 0.031	0.358 ± 0.043	0.342 ± 0.065
$k_c/\text{M}^{-1} \text{ s}^{-1}$	2.67 ± 0.10	8.97 ± 0.14	9.42 ± 0.21

Table 3. Second-Order Rate Constants Obtained for the Reaction of $\text{HNO}_2 + \text{H}_2\text{O}_2$ at pH 3.87 and 0°C . $[\text{H}_2\text{O}_2]_0 = 5.0 \times 10^{-3} \text{ M}$, $[\text{N(II)}]_0 = 5.0 \times 10^{-5} \text{ M}$

[X ⁻]	$k'/\text{M}^{-1} \text{ s}^{-1}$		
	Cl ⁻	Br ⁻	SCN ⁻
0.00	1.85×10^{-2}	1.85×10^{-2}	1.85×10^{-2}
0.10	3.15×10^{-2}	5.92×10^{-2}	5.46×10^{-2}
0.20	4.66×10^{-2}	9.38×10^{-2}	8.89×10^{-2}
0.30	5.81×10^{-2}	13.4×10^{-2}	12.3×10^{-2}
0.40	6.73×10^{-2}	16.8×10^{-2}	15.8×10^{-2}
0.50	7.70×10^{-2}	21.0×10^{-2}	18.9×10^{-2}
$k_0/\text{M}^{-1} \text{ s}^{-1}$	$(2.05 \pm 0.17) \times 10^{-2}$	$(1.93 \pm 0.15) \times 10^{-2}$	$(1.99 \pm 0.12) \times 10^{-2}$
$k_c/\text{M}^{-1} \text{ s}^{-1}$	0.118 ± 0.006	0.379 ± 0.005	0.342 ± 0.004

A strong pH dependence of k' in the Tables 1-3 suggests that the reaction is acid-catalysed. Also significant catalytic effects of added anions were observed for Cl⁻, Br⁻, and SCN⁻ at each pH studied while no catalytic effect was observed for NO₃⁻ and ClO₄⁻ at pH 2.08. The effect of ClO₄⁻ can be deduced from the data of NO₃⁻ because for those experiments the total concentrations of two ions ([NO₃⁻] + [ClO₄⁻]) were kept constant. At constant pH, k' increased linearly with the concentrations of added anions for Cl⁻, Br⁻ and SCN⁻ (see Figure 3).

$$k' = k_0 + k_c[X^-] \quad (4)$$

The slope (k_c) indicates catalytic efficiency and Figure 3 shows that it is on the order of $\text{SCN}^- \approx \text{Br}^- > \text{Cl}^-$.

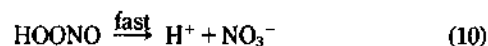
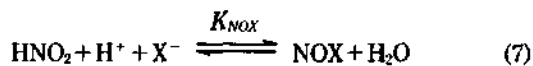
Discussion

The reaction mechanism which is consistent with the observed kinetic behavior and other known properties of nitrous acid is given as follows.

**Table 4.** Calculated Values of k_1/K'_a ($\text{M}^{-2} \text{ s}^{-1}$) and k_2 ($\text{M}^{-1} \text{ s}^{-1}$)

pH	2.08	3.03	3.87	average
k_1/K'_a (Cl ⁻)	776	666	881	
(Br ⁻)	816	650	829	
(SCN ⁻)	801	621	855	766 ± 32^a
k_2 (NOCl)	7.03×10^6	8.65×10^6	9.05×10^6	8.24×10^6
(NOBr)	7.22×10^6	7.40×10^6	7.40×10^6	7.34×10^6
(NOSCN)	4.03×10^2	3.69×10^2	3.17×10^2	3.63×10^2

^aAverage of 9 values listed with a standard deviation.



Here we simply presumed the nitrous acidium ion as an actual nitrosating reagent although we cannot kinetically distinguish this ion from nitrosonium ion. Equilibrium constants are defined as $K_a = \alpha_{\text{H}^+}[\text{NO}_2^-]/[\text{HNO}_2]$, $K'_a = \alpha_{\text{H}^+}[\text{HNO}_2]/[\text{H}_2\text{NO}_2^+]$ and $K_{\text{NOX}} = [\text{NOX}]/[\text{HNO}_2]\alpha_{\text{H}^+}[\text{X}^-]$. In these expressions hydrogen ion activity α_{H^+} rather than H^+ concentration is employed because the acidity was measured as pH. Previously reported pK_a values¹⁵ are in the range of 3.1-3.5 and a recommended thermodynamic value of pK_a° is 3.148 ($K_a^\circ = 7.11 \times 10^{-4}$) at zero ionic strength at 25°C .¹⁶ The value of K_a° at 0°C is calculated to be 4.14×10^{-4} by using $\Delta H^\circ = 14.6 \text{ kJ mol}^{-1}$ for the ionization of HNO_2 .¹⁷ The K_a value in our experimental condition could be estimated from the following equation under the assumption that the nonionic species have a unit activity coefficient.⁷

$$K_a^\circ = \alpha_{\text{H}^+}[\text{NO}_2^-]\gamma/[\text{HNO}_2] = \gamma K_a$$

If we choose the activity coefficient of NO_2^- , γ , as 0.64 for the solution of 0.5 M ionic strength at 0°C ,¹⁸ then the K_a value is calculated to be 6.47×10^{-4} . No reliable K'_a value is available yet. Bhattacharyya and Veeraraghavan⁴ reported K'_a defined in the form of $[\text{H}^+][\text{HNO}_2]/[\text{H}_2\text{NO}_2^+]$ as $8.62 \times 10^{-3} \text{ M}$ at 25°C from their kinetic measurements. However, it has been criticized by other investigators that this value is too small to be compatible with many published kinetic and equilibrium studies of nitrous acid in acidic solutions.^{6,7,19} Haim *et al.*⁹ suggested that K'_a must be bigger than 1. K_{NOX} values defined as $[\text{NOX}]/[\text{HNO}_2][\text{H}^+][\text{X}^-]$ are known to be 5.6×10^{-4} , 2.2×10^{-2} and 46.3 in units of M^{-2} at 0°C for K_{NOCl} , K_{NOBr} and K_{NOSCN} , respectively.²⁰

By assuming that the equilibria of reaction (5)-(7) are established rapidly and the reaction (8) and (9) are the rate-determining steps, we can write the rate equation:

$$\text{Rate} = (k_1[\text{H}_2\text{NO}_2^+] + k_2[\text{NOX}]) [\text{H}_2\text{O}_2] \\ = (k_1/K'_a + k_2K_{\text{NOX}}[\text{X}^-]) \alpha_{\text{H}^+}[\text{HNO}_2][\text{H}_2\text{O}_2] \quad (11)$$

$$= (k_1/K'_a + k_2K_{\text{NOX}}[\text{X}^-]) \{ \alpha_{\text{H}^+}/(1 + K_a/\alpha_{\text{H}^+}) \} \\ [\text{H}_2\text{O}_2][\text{N(II)}] \quad (12)$$

where $[N(III)] = (1 + K_a/\alpha_{H^+})[HNO_2]$ is used because the concentrations of other N(III) species are negligibly small compared to the sum of concentrations of HNO_2 and NO_2^- in our experimental conditions.²¹ Eq. (11) corresponds to the sum of Eq. (1) and (2) which represent uncatalysed and catalysed portion of the reaction rate by added anions. From Eq. (3), (4) and (12), observed k_o and k_c values can be expressed as $(k_1/K_a')\{\alpha_{H^+}/(1+K_a/\alpha_{H^+})\}$ and $k_2K_{NOX}\{\alpha_{H^+}/(1+K_a/\alpha_{H^+})\}$, respectively. Since K_a and K_{NOX} values are known, we can obtain k_2 from k_c . However, we cannot obtain k_1 values from k_o because K_a' value is not known accurately. We can only obtain apparent third order rate constant in Eq. (1) which is equal to k_1/K_a' . Table 4 shows k_1/K_a' and k_2 values for each anion at three different pHs and the average values.

Previously reported values of k_1/K_a' converted to the values for 0°C using Arrhenius activation energy⁷ of 55.6 kJ mol⁻¹ are 590¹⁶ and 809 M⁻²s⁻¹.¹⁷ The average value of our results 766 M⁻²s⁻¹ is within the range of earlier measurements although the experimental conditions and methods are different.

The k_2 values show the reactivity order of NOCl > NOBr > NOSCN as is observed in many other nitrosation reactions. This reactivity sequence is expected from the relative nucleophilicities of Cl⁻, Br⁻ and SCN⁻, and is also predicted by MO calculations using frontier orbital theory.²³

The k_2 value for NOCl obtained in our study is far smaller than the calculated value for the encounter limit (3.4×10^9 M⁻¹s⁻¹ at 0°C for reactions in water²⁴). The second order rate constants obtained for diazotisation of aromatic primary amines with $pK_a > ca. 3$ by NOCl and NOBr are in the region of 10^9 M⁻¹s⁻¹ at 25°C and are regarded as encounter limit.²⁴ On the other hand, Castro *et al.* suggested that the encounter limit for aliphatic amines is $ca. 2 \times 10^7$ M⁻¹s⁻¹ from their experimental results at 25°C and that the extra reactivity of the aromatic amines arises in some other way.²⁵ More recent studies, *e.g.*, reaction of ammonia with NOBr,²⁶ reactions of thiols with NOCl²⁷ and reactions of sarcosine and proline with NOSCN,²⁸ also showed that second order rate constants are within the range of $1-3 \times 10^7$ M⁻¹s⁻¹ at 25°C. If the encounter limit is in the region of 10^7 M⁻¹s⁻¹, then k_2 value for NOCl in our study is close to or at the encounter limit.

The reactivity of NOCl in our study is *ca.* 10 times greater than that of NOBr which is comparable to the reactivity ratio of *ca.* 20 for S-nitrosation of thiols whose nitrosation rates are similar to or slightly less than that of H₂O₂.²⁷ However, for more reactive aniline derivatives, this ratio is *ca.* 1 since the reactions of both NOCl and NOBr are at encounter limit as mentioned above.^{8,24} Also the reactivity ratio of NOBr to NOSCN in our study is *ca.* 10³ while this ratio is 10² or less for many N- or S-nitrosations.^{8,27}

Finally, it is worth to check the validity of the assumption we made to derive the rate Eq. (11), *i.e.*, the reaction (9) is rate-determining with the rapid equilibrium of the reaction (7). The literature values of rate constants for the reverse reaction of reaction (7), k_{-7} , are 1.8×10^6 , 5.3×10^4 and 32 s⁻¹ for NOCl, NOBr and NOSCN, respectively.^{9c} The highest values of pseudo-first-order rate constants for the reaction (9), $k_2[H_2O_2]$, in our experimental conditions at pH 3.87 are 4.5×10^4 , 3.7×10^3 and 1.6 s⁻¹, for NOCl, NOBr and NOSCN, res-

pectively. These $k_2[H_2O_2]$ values are smaller by a factor of 5 at pH 3.03 and by a factor of 20 at pH 2.08. Thus, the ratio of $k_{-7}/k_2[H_2O_2]$ is high enough so that our assumption is valid for all experimental conditions.

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21. Presence of NO⁺, H₂NO₂⁺, N₂O₃, and NOX and all negligible; $[NO^+]/[H^+][HNO_2] = 3.0 \times 10^{-5} - 7.8 \times 10^{-9}$ M⁻¹,¹⁵ $[N_2O_3]/[HNO_2]^2 = 3.03 \times 10^{-3}$ M⁻¹,²² $[H_2NO_2^+]/[H^+][HNO_2] < 1$ M⁻¹.¹⁹ The highest concentration of NOX in our experimental condition is $[NOSCN]/[NHO_2] = K_{NOSCN} \alpha_{H^+} [SCN^-] = 3.85 \times 10^{-2} < 1$ at pH 2.08 and $[SCN^-] = 0.1$ M.^{20c}
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Regioselectivity in the Cycloaddition Reactions of *t*-Butyl Trimethylsilyl Thioketone with 1,3-Butadienes

Kyung-Tae Kang*, Chi Hyo Park, and Ung Chan Yoon†

Department of Chemical Education and †Department of Chemistry, Pusan National University, Pusan 609-735. Received August 22, 1991

Thermal cycloaddition of *t*-butyl trimethylsilyl thioketone (**1**) with 2-substituted dienes such as isoprene and 2-trimethylsilyloxy-1,3-butadiene occurred smoothly at 80°C to afford regioisomeric mixtures of cycloadducts. On the other hand, similar treatment of **1** with 1-substituted dienes such as *trans*-1,3-pentadiene, 1-methoxy- and 1-acetoxy-1,3-butadiene and Danishefsky's diene afforded a single regioisomeric adduct, respectively. Protodesilylation of the silylated adducts **8** and **11** could also be performed with ease.

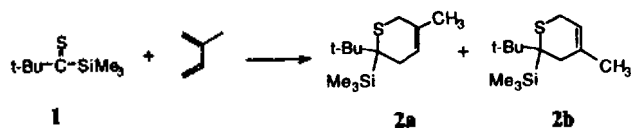
Introduction

Thioacylsilanes have received increasing attention in recent years due to the high reactivity of the carbon-sulfur double bond, which makes possible the synthesis of a variety of compounds, containing the Si-C-S unit.¹ Since these compounds undergo facile desilylation with fluoride ion, thioacylsilanes can be used as synthetic equivalents of unstable thioaldehydes and thiocarbonyl anions.

The reactivity and diastereoselectivity in the cycloaddition of thioacylsilanes with dienes were studied.^{1b,c} However, the regioselectivity in the cycloaddition was not explored.² Here we describe our results concerning the regioselectivity shown in the reaction of a stable aliphatic thioacylsilane, *t*-butyl trimethylsilyl thioketone (**1**) with unsymmetrical 1,3-butadienes, and further protodesilylation of some silylated cycloadducts.

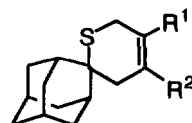
Results and Discussion

Cycloaddition Reactions of 1 with 2-Substituted Butadienes. When a mixture of *t*-butyl trimethylsilyl thioketone (**1**) and 5-fold excess of isoprene in benzene was heated to 80°C in a sealed tube, the characteristic blue color of **1** completely disappeared in about 6 h. After purification by preparative tlc (silica gel, *n*-hexane : ether = 8 : 1), a mixture of inseparable regioisomers (**2a** and **2b**) was obtained in 85% yield.



The cycloadducts were identified to be 5-methyl-2-*t*-butyl-2-trimethylsilyl-3,6-dihydro-2*H*-thiopyran **2a** and 4-methyl analog **2b** on the basis of spectral data. The mass spectral molecular ion at *m/e* 242 as well as fragment ions at *m/e* 185 ($M^+ - t\text{-bu}$) and 137 ($M^+ - \text{Me}_3\text{Si-S}$) supported the given structure **2a** and/or its regioisomer **2b**. In the 270 MHz ¹H-NMR spectrum, the trimethylsilyl and *t*-butyl protons of **2a** and **2b** appear at δ 0.14, 1.03 and δ 0.16, 1.04, respectively. The methyl protons are not resolved, and appear at δ 1.76 and split into a doublet (*J* = 1.5 Hz) due to allylic coupling with the vinylic proton. The C-6 methylene protons of **2a** are resolved completely as an AB quartet (*J* = 15.2 Hz) centered at δ 2.76 and 2.91 while those of **2b** appear as a multiplet at δ 2.95-3.01. The ratio of **2a** and **2b** was determined to be 80 : 20 by ¹H-NMR.

In the ¹³C-NMR spectrum, two pairs of signals due to double-bond carbons of the cycloadducts (**2a** and **2b**) appear at δ 124.30, 133.59 and δ 119.25, 136.59, respectively, and the ratio is approximately 80 : 20. The chemical shifts are very similar to those of the cycloadducts of adamantanethione with isoprene, **3a** [δ 121.2 and 129.9] and **3b** [δ 116.8 and 134.0].³ These results suggest that the major regioisomer is **2a**.



3a, R¹ = CH₃, R² = H
3b, R¹ = H, R² = CH₃

The cycloaddition of **1** with 2-trimethylsilyloxy-1,3-butadiene was performed in benzene at 80°C for 3 h, and the crude cycloadducts (**4a** and **4b**) were treated with 1 N HCl. After chromatography on silica gel, a mixture of regioisomers